TITLE OF THE INVENTION

METAL BELT AND COATED BELT

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the benefit of priority from the prior Japanese Patent Applications No. 2002-350313, filed December 2, 2002; and No. 2002-350314, filed December 2, 2002, the entire contents of both of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an endless metal belt, and a coated belt obtained by coating the metal belt, which are used for image forming apparatuses, such as copying machines, facsimiles, and laser beam printers.

2. Description of the Related Art

To meet demands such as miniaturization, reduction in the power consumption, and increase in the speed of printing and copying of image forming apparatuses, there has been adopted a belt fixing method, in which an endless fixing belt (endless belt or tube) is driven to be rotated instead of a fixing roller. A fixing belt has the advantage that waiting time after turning on the power is reduced, since a toner image on a transfer member can be almost directly heated and fixed, with only a thin belt intervening, by bringing heating means into contact with an internal surface of

the fixing belt.

In such a fixing belt, a release layer is formed
by coating directly, or with an elastic layer interven-
ing, on an endless metal belt base material. In most
cases, a release layer is made of a heat-resistant
resin having excellent heat-resistance and releasing
property, such as fluoroplastics. Since a release
layer made of heat-resistant resin lacks elasticity,
in most cases an elastic layer is disposed between the
metal belt base material and the release layer, to
improve fixing property and image quality. If the
release layer is a rubber layer having elasticity and
releasing property, such as a silicone rubber layer,
an intermediate elastic layer can be omitted. As a
transfer belt, a charged belt, and a conveyer belt,
used is an endless belt made of a metal belt base
material alone, or of a metal belt base material and
a release layer.

USP 6,564,033, Jpn. Pat. Appln. KOKAI Pub.
No. 2002-241984 and Jpn. Pat. Appln. KOKAI Pub.
No. 2002-148975 disclose an endless nickel belt formed
as a metal belt base material by using electroforming.

USP 6,564,033 discloses an electroformed nickel
belt, in which a plane (200) is preferentially grown,
in which the electroformed nickel has a crystal
orientation ratio $I_{(200)}/I_{(111)}$ of 3 or more,
preferably 8 or more, and a carbon content of

electroformed nickel is not more than 0.08 wt%.

Jpn. Pat. Appln. KOKAI Pub. No. 2002-241984 discloses an electroformed nickel belt containing at least one additive element selected from the group consisting of thallium, lead, bismuth, tin, calcium, zinc, aluminum, silicon, and antimony.

Jpn. Pat. Appln. KOKAI Pub. No. 2002-148975 discloses an electroformed nickel belt whose carbon content is 0.01 to 0.1 wt%.

However, conventional nickel belts do not have sufficient fatigue strength at high temperature, and lack durability. In the belt fixing method, a belt is repeatedly bent in a fixing nip part and an inlet and outlet thereof with rotation of the belt itself, and torsion is caused on the belt by difference in the peripheral speed. Therefore, the belt tends to be mechanically fatigued, and has a problem in heat resistance and durability. For example, its endurance time is shortened by increasing the fixing temperature. In particular, since the fixing nip part of a high-speed printer is wide and has a high pressing force, mechanical force applied on the belt increases, and a high fixing temperature is set. Therefore, the conventional belts tend to be broken for a relatively short time, and must be replaced with high frequency.

Further, in a belt having a high carbon content, a plating film has an increased internal stress.

Therefore, its releasing property decreases, an electroformed product is not easily removed from a matrix, and a part of the electroformed product may be separated from the matrix during electrolysis due to

5 excessive internal stress.

BRIEF SUMMARY OF THE INVENTION

The object of the present invention is to provide a long-life metal belt and a coated belt, which have an excellent durability, an electroformed product of which

10 can be easily removed from an electroforming matrix, and which prevent partial separation from the matrix.

(Metal Belt)

A metal belt being formed to be endless by electroforming, and mainly containing nickel, wherein

15 the belt comprises a crystal orientation in which a crystal orientation ratio $I_{(200)}/I_{(111)}$ is not less than 80 and not more than 250.

Properties necessary for a fixing belt are basic properties, such as heat resistance to a maximum

20 heating temperature and mechanical strength. In addition, to further increase durability, a fixing belt is required to have an excellent fatigue strength at high temperature. In the metal belt of the present invention, a plane (200) is preferentially grown, and

25 thereby fatigue resistance, that is, durability at high temperature is improved. A belt made by preferentially growing the plane (200) in crystal growth resists

deterioration of flexibility and strength of the belt even if it is subjected to high temperature, which is advantageous as a fixing belt used at high temperature.

In the present invention, "the plane (200) is preferentially grown" means that the crystal is preferentially grown to a plane (200) parallel to the surface of a matrix. The crystal orientation ratio $I_{(200)}/I_{(111)}$ is defined as a ratio (peak strength ratio) of peak strength of a surface (111) to peak strength of a plane (200) measured by wide-angle X-ray diffraction. A d value of the plane (200) is 0.17620 nm, and a d value of the plane (111) is 0.20340 nm.

Further, in the present invention, the crystal orientation ratio $I_{(200)}/I_{(111)}$ is set to from 80 to 250 inclusive 80 and 250, and thereby a sufficient durability is ensured against a high-temperature heating cycle. The inventor(s) of the present invention have diligently researched an influence of the crystal orientation ratio $I_{(200)}/I_{(111)}$ on durability of belt, and consequently have obtained new information as to correlation between them as shown in FIG. 3 and Table 1. According to the information, the number of repetition durability times of the belt obtained by a heat fatigue test is about 130,000 in samples H and I, whose crystal orientation ratios $I_{(200)}/I_{(111)}$ are less than 50, and does not reach

200,000 being the acceptable quality level. However,
the numbers of repetition durability times of samples
A-G, whose crystal orientation ratios $I_{(200)}/I_{(111)}$ are
113, 114, 132, 147, 169, 198 and 246, respectively, are

5   much larger than 200,000, the acceptable quality level.

The crystal orientation ratio $I_{(200)}/I_{(111)}$ is
influenced by various parameters, such as the
composition of nickel pellet being starting material,
the composition and the temperature of nickel bath,

10   the current density, and the state of surface of a
matrix, etc. Therefore, in prior art, it is difficult
to intentionally set the crystal orientation ratio to
a desired value at the manufacturing stage. If the
crystal orientation ratio $I_{(200)}/I_{(111)}$ is small, in

15   particular, 50 or less, the belt tends to be fatigued
by heat cycles, and has insufficient durability.
Patent documents say that sulfur and organic substances
obtained from a brightener in an electrolytic bath are
deposited as eutectoid together with crystal growth

20   of nickel, and it causes disadvantages in the high-
temperature durability of the belt. In addition,
electroformed nickel tends to have a cristallite
structure and thus has a high hardness, and it is
inferred that it can cause a problem with flexibility

25   of the belt. The inventor(s) of the present invention
inferred that a crystal structure with a small crystal
orientation ratio $I_{(200)}/I_{(111)}$ is susceptible to

thermal degradation.

In the present invention, a carbon content of
a metal belt mainly composed of nickel is 0.03 to
0.10 wt%. By restricting the carbon content within
5   the above range, it is possible to more easily obtain
an electroformed nickel belt whose hardness and
strength do not deteriorate due to thermal aging, while
a standard hardness required as an endless metal belt
base material is maintained. If the carbon content is
10   less than 0.03 wt%, the crystal orientation ratio is
lowered and the durability is reduced. The carbon
content exceeding 0.10 wt% increases the internal
stress of the plating film and lowers the releasing
property. Therefore, it may be difficult to remove
15   an electroformed product from a matrix, or a part of
the electroformed product may be separated from the
matrix during electrolysis. However, if a matrix
releasing technique is further improved, it is inferred
that a belt with a carbon content up to about 0.14 wt%
20   can be manufactured. If the carbon contents exceeds
0.14 wt%, the plating film itself is not soundly
formed. The correlation between the carbon content and
the number of repetition durability times is as shown
in FIG. 4 and Table 1 shown later.

25   Further, there is a correlation between the carbon
content and the crystal orientation ratio as shown in
FIG. 5 and Table 1. The crystal orientation ratio

depends heavily on the carbon content. As shown in FIG. 5, the peak value of the crystal orientation ratio (the peak value is estimated to be about 250 since the actual measured peak value was 246) exists in the vicinity of a point where the carbon content is 0.06 wt%. The crystal orientation ratio lowers, with the carbon content of any value other than the peak value. If the belt has an excessive carbon content much higher than 0.10 wt%, it is inferred that the crystal orientation ratio is lower than 80. Further, if the carbon content exceeds 0.10%, the internal stress increases, crack occurs, and thus a part of the product may be separated from the matrix. Therefore, a stable crystal growth cannot be expected.

The metal belt (or metal base material) of the present invention is substantially free of manganese (0.00 wt%; lower than limit of detection). This is because containing manganese prevents increases in the crystal orientation ratio and in fatigue resistance under high-temperature heat cycles, although the reason is unclear.

The metal belt often contains impurities, such as sulfur, cobalt and carbon generated from components of a nickel plating bath. If the belt contains a large amount of impurities such as sulfur and cobalt, it is difficult to grow crystals of nickel in orderly layers in plating, and the crystal orientation ratio

decreases. Adjusting the content of each of the
impurities can further improve the properties of the
metal belt.

The sulfur content of the metal belt is preferably
5   adjusted to be less than 0.03 wt%. The sulfur content
is more preferably 0.01 wt% or less. If the sulfur
content is too high, sulfur is deposited on the grain
boundary of nickel under continuous heating conditions,
and causes decrease in hardness and strength. Although
10   the lower limit of the sulfur content is 0 wt%
(0.00 wt%; lower than limit of detection), in the case
of using sulfur-containing compound (for example,
a primary brightener) as an ingredient of the nickel
plating bath, generally the sulfur content is 0.01 to
15   0.09 wt%, 0.001 to 0.009 wt% if reduced as much as
possible. In the case of using an electrolytic bath of
sulfamic acid without using a brightener, the sulfur
content is 0.0001 to 0.0009 wt%.

The sulfur content can be reduced by reducing the
20   amount of use of sulfur-containing compounds, such as
a brightener. Although sulfur in the metal belt is an
indispensable component which reduces electrodeposition
stress and improves manufacturing accuracy, it also
damages the flexibility and the elasticity at high
25   temperature and has a great influence on break due to
metal fatigue. If the belt contains too much sulfur,
there are cases where sulfur forms a thin brittle film

around the nickel grain boundary at high temperature and makes the grain boundary of the electroformed nickel discontinuous. In such a case, the belt may be subject to brittle fracture. In the meantime, if the sulfur content is too low, the releasing property from the matrix and the strength of the belt may lowers. The normal lower limit of the sulfur content is 0.001 to 0.009 wt%.

Nickel or nickel alloy, whose carbon content and sulfur content fall within the above respective ranges, and which is substantially free of manganese and cobalt being an inevitable impurity element, tends to have a crystal structure, in which a plane (200) is preferentially grown in crystal growth of the electroformed nickel and the crystal orientation ratio $I_{(200)}/I_{(111)}$ is 100 or more. Further, if the sulfur content is low, a plane (200) is more likely to be preferentially grown in crystal growth.

The normal content of the other inevitable impurities is 0.01 wt% or less. In the present invention, the content of the inevitable impurities other than nickel is preferably reduced as much as possible. If the crystal orientation ratio $I_{(200)}/I_{(111)}$ is too low, the durability tends to decrease.

The metal belt is manufactured by electroforming process, using a matrix of stainless steel, etc. as

a cathode. In this process, a publicly-known nickel

electrolytic bath such as sulfamic acid bath can be

used as an electrolytic bath, and additives such as a

pH adjuster, pit inhibitor and brightener may be added

5   to the bath. An example of the nickel electrolytic

bath is a nickel electrolytic solution containing

nickel sulfamate as a main component, and containing

0-30 g/l of nickel chloride or nickel bromide, and

30-45 g/l of boric acid. The concentration of

10   sulfamate nickel can be selected from low to high

concentrations according to the purpose. Nickel

sulfamate tetrahydrate of 450 g/l is called a normal

bath, and that of 600 g/l is called a nickel speed bath

or a high-concentration bath. A bath of a concentra-

15   tion lower or higher than the above can be used.

By controlling the temperature of the electrolytic

bath and the cathode current density and the like,

an electroformed nickel made of a desired nickel or

nickel alloy can be obtained. The electroforming

20   process is preferably performed with an electrolytic

bath temperature of about 45 to 60℃, and a cathode

current density of about 1 to 10 A/dm^2, although they

vary according to the electrolytic bath to be used.

Additives called a primary brightener (stress reducing

25   agent) including saccharin, sodium benzenesulfonate,

and sodium naphthalenesulfonate, etc. and a secondary

brightener including 2-butyne-1,4-diol, coumarin, and

diethyltriamine, etc. are added to the electrolyte bath. Thereby, the stress in electrodeposition of the electroformed nickel is reduced, and the molding accuracy is improved. By adjusting the amounts of the additives added in this process, the sulfur content and the carbon content in the electroformed nickel can be set within the above ranges. The contents of the deposited sulfur and carbon can be adjusted by the process conditions, such as concentrations of the primary and secondary brighteners in the bath, the current density, and the temperature of the bath.

To increase the crystal orientation ratio $I_{(200)}/I_{(111)}$, it is necessary to use a specific bath composition together with a specific manufacturing process. The specific bath composition contains predetermined amounts of the primary brightener and the secondary brightner, is substantially free of manganese, and cobalt being inevitable impurity limited to be less than 5 mg/l. In the manufacturing process, the current density in electroforming is properly adjusted, and thereby a plane (200) can be preferentially grown, and the peak intensity of the plane (200) measured by X-ray diffraction is enhanced.

The thickness of the metal belt is greater than a skin depth expressed by the formula below, preferably 1 μm to 100 μm. The skin depth σ [m] is represented by the formula below, with the frequency f (Hz),

magnetic permeability μ, and specific resistance
ρ (Ωm) of an exciting circuit:

$$\sigma \text{ [m]} = 503 \times (\rho / f \mu)^{1/2}$$

This shows absorption depth of electromagnetic

5   waves used in electromagnetic induction. The strength

of electromagnetic waves at a deeper portion is not

more than 1/e. Conversely, most energy is absorbed up

to this depth. If the thickness of the belt is less

than 1 μm, the belt cannot completely absorb most of

10   electromagnetic energy, and the efficiency decreases.

In the meantime, a metal belt having a thickness

greater than 100 μm has a high stiffness and a low

flexibility, thus it is difficult to be used as a

rotating member. If the belt is used in a belt fixing

15   method using a ceramic heater, the thickness of the

belt is preferably not more than 100 μm, more

preferably not more than 50 μm, and most preferably

not more than 20 μm, to reduce the heat capacity and

improve its quick-start property.

20   It is proved, by observation of the surface etched

after ground, that the crystal of the metal belt varies

according to the heating temperature and the heating

time. If the crystal orientation ratio is high, the

crystal becomes resistant to change, less variable

25   in hardness, and less prone to decrease in strength.

The greater change of the crystal and change in the

hardness under high-temperature conditions deteriorate

the fatigue resistance.

(Coated Belt)

The coated belt of the present invention is formed in an endless form by electroforming, with a crystal orientation ratio $I_{(200)}/I_{(111)}$ of from 80 to 250 inclusive 80 and 250, and comprises a metal base material mainly containing nickel, and a release layer formed on an external periphery of the metal base material with at least one elastic layer intervening therebetween. The metal base material further contains 0.03 to 0.10 wt% of carbon.

As the release layer, preferable are fluorocarbon resin such as PFA (tetrafluoroethylene/perfluoroalkylether copolymer), PTFE (polytetrafluoroethylene), FEP (tetrafluoroethylene/hexafluoropropylene copolymer), silicone resin, fluorosilicone rubber, fluorine rubber and silicone rubber. In particular, PFA is preferred. According to necessity, the release layer may contain a conductive agent, such as carbon and tin oxide and so on, in an amount not more than 10 wt% of the release layer.

The thickness of the release layer is preferably 1 μm to 100 μm. If the thickness of the release layer is less than 1 μm, there may be the cases where a badly released portion is generated due to irregular coating of the coating and durability is insufficient.

In the meantime, if the thickness of the release layer exceeds 100 μm, there are the cases where the heat conductivity deteriorates. In particular, in a resin-based release layer, the hardness is so increased that the elastic layer described later produces no effect.

If the release layer is manufactured by a publicly-known method, for example, if it is formed of a fluorocarbon resin-based material, it may be formed by a method of coating with a dispersed coating of fluorocarbon resin powder and drying and baking it, or a method of coating with fluorocarbon resin tubed in advance and adhering it. The release layer of rubber material can be formed by a method of injecting liquid material into a mold and curing it by heating, a method of curing liquid material by heating after extrusion, or a method of curing by heating after injection molding, etc.

Further, it is possible to form the elastic layer and the release layer simultaneously, by using a method of mounting a tube with primer-treated internal surface and an electroformed nickel belt with a primer-treated surface in a cylindrical mold, injecting liquid silicone rubber into a gap between the tube and the electroformed nickel belt, and curing and adhering the rubber by heating.

Although the elastic layer is not an indispensable constituent element of the present invention, it is

preferably provided to secure a certain amount of nip width and heat capacity. As the material of the elastic layer, preferred are silicone rubber, fluorine rubber and fluorosilicone rubber, in particular,

5   silicone rubber. Examples of the silicone rubber used for the elastic layer are polydimethylsiloxane, polymethyltrifluoropropylsiloxane, polymethylvinylsiloxane, polytrifluoropropylvinylsiloxane,

10   polymethylphenylsiloxane, polyphenylvinylsiloxane, and copolymers of the above polysiloxane. As occasion demands, the elastic layer main contain a reinforcing filler such as dry silica and wet silica, calcium carbonate, quartz powder, zirconium silicate, clay

15   (aluminum silicate), talc (hydrated magnesium silicate), alumina (aluminum oxide), and colcothar (ferric oxide), etc.

Because favorable fixed image quality is obtained, the thickness of the elastic layer is not less than

20   10 μm, preferably not less than 50 μm, and not more than 1000 μm, preferably not more than 500 μm. If a color image is printed, in particular, a photograph image, a solid image is formed over a wide area on the transfer member. In such a case, if the heating

25   surface (the release layer) cannot follow the unevenness of the transfer member or the unevenness of the toner layer, irregular heating is caused, and

brightness irregularity occurs on a part of the image with much or small heat transferred. Specifically, a part with much heat transferred has high brightness, while a part with small heat transferred has low brightness. If the elastic layer is too thin, since the heating surface cannot completely follow the unevenness of the transfer member or toner layer, image brightness irregularity may occur. Further, if the elastic layer is too thick, the heat resistance of the elastic layer is increased, and it may be difficult to realize quick start.

Although the sliding layer is not an indispensable constituent element of the present invention, it is preferably provided to reduce the driving torque to operate the fixing apparatus. Examples of the material of the sliding layer are polyimide resin, polyamideimide resin, phenol resin, fluorocarbon resin, PEEK (polyetheretherketone resin) resin, PES (polyethersulfone) resin, PPS (polyphenylene sulfide) resin, PFA (tetrafluoroethylene/perfluoroalkylether copolymer) resin, PTFE (polytetrafluoroethylene) resin, FEP (tetrafluoroethylene/hexafluoropropylene copolymer) resin, and LCP (liquid crystal polyester) resin, etc. As the occasion demands, the sliding layer may contain a sliding agent, such as fluorocarbon resin powder, graphite, and molybdenum disulfide. The sliding layer can be formed by, for example, a method of coating,

drying and curing liquid material, or a method of adhering a tubed material. A sliding layer can provide heat insulation to prevent the heat generated on the metal base material as a heat-generating layer from

5 propagating to the inside of the belt, without increasing the heat capacity of the coating belt too much. Therefore, in comparison with the case of having no sliding layer, the heat supply efficiency to the transfer member side is improved, and the power

10 consumption can be reduced. Further, it is possible to shorten the rise time.

The thickness of the sliding layer is preferably 5 μm to 100 μm. If the thickness of the sliding layer is less than 5 μm, the durability may be insufficient.

15 If the sliding layer has a thickness exceeding 100 μm, the heat capacity of the belt and the rise time may be increased.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a cross-sectional view of a coated belt

20 of the present invention.

FIG. 2 is a diagram illustrating a test piece used for an evaluation test of a metal belt of the present invention.

FIG. 3 is a characteristic diagram illustrating

25 a relationship between a crystal orientation ratio and number of repetition durability times in the metal belt of the present invention.

FIG. 4 is a characteristic diagram illustrating a relationship between a carbon content and number of repetition durability times in the metal belt of the present invention.

5 FIG. 5 is a characteristic diagram illustrating a relationship between the carbon content and the crystal orientation ratio $I_{(200)}/I_{(111)}$ in the metal belt of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

10 Various preferable examples of the present invention will now be described with reference to attached drawings.

In electroforming, a matrix (electrotype mold, mold) having conductivity, such as a cylindrical matrix

15 made of stainless steel, is used as a cathode, and a nickel plating film is formed on the surface of the matrix by subjecting it to electroplating with a nickel plating bath. The plating film is exfoliated (removed) from the matrix, and used as a product. If the matrix

20 is made of metal, it is subjected to surface treating for exfoliation. If the matrix is made of nonmetal, it is subjected to conductivity treatment for plating.

As shown in FIG. 1, a coated belt 10 has a complex structure, comprising a metal base material 1 made of

25 an endless metal belt serving as a base layer, an elastic layer 2 provided on an external surface of the base material 1, a release layer 3 covering an external

surface of the elastic layer 2, and a sliding layer 4
covering an internal surface of the base material 1.
In the coated belt 10, the sliding layer 4 is disposed
on the internal surface side (belt guiding surface

5   side), and the release layer 3 is disposed on the
external surface side (pressing roller surface side).
A primer layer (not shown) may be provided for adhesion
between the metal base material 1 and the elastic layer
2, between the elastic layer 2 and the release layer 3,

10   or between the metal base material 1 and the sliding
layer 4. As the primer layer, publicly-known
material can be used, such as silicone, epoxy, and
polyamideimide, and the thickness of the primer layer
is about 1 to 30 μm.

15   (Metal Belt: metal base material)

The metal base material 1 corresponds to the
metal belt of the present invention. The base material
1 is formed to be endless by electroforming, and has
a crystal orientation property in which the crystal

20   orientation ratio $I_{(200)}/I_{(111)}$ is from 80 to 250
inclusive 80 and 250 and a plane (200) is preferen-
tially grown. Further, the metal base material 1
contains carbon of 0.03 to 0.10 wt%. Although the
metal base material 1 can be used singly as a fixing

25   belt, in normal times it is used as a coated belt
10 made by forming the release layer 3 made of
fluorocarbon resin and the like on an external

peripheral surface of the base material 1 directly, or
with the elastic layer 2 of silicone rubber and the
like intervening therebetween. The thickness, width
and internal diameter of the metal belt can be set

5   according to its uses, and are not limited to
particular values. Generally, the thickness is 10 to
1000 μm, preferably 15 to 500 μm, and more preferably
20 to 100 μm. In view of balance between the heat
capacity, heat conductivity, mechanical strength and

10   flexibility, etc., the thickness is most preferably 30
to 80 μm. If it is used as a fixing belt or a
transfer belt, etc. in an electrophotographic copying
machine, the width of the belt can be determined
according to the width of the transfer material such as

15   transfer paper.

Brighteners are generally classified into primary
brighteners and secondary brighteners. To obtain a
high brightness, both of them are often used together.
Among them, primary brighteners are organic compounds

20   having a structure of $=C-SO_2-$, and examples
thereof are sulfonate (aromatic sulfonate such as
1,3,6-naphthalene-trisulfonic acid trisodium salt),
sulfoneimide (for example, saccharin), sulfoneamide,
and sulfinic acid, etc. Among them, aromatic sulfonate

25   is preferably used.

Examples of secondary brighteners are organic
compounds having a structure selected from C=O, C=C,

$C \equiv N$, $C=N$, $C \equiv C$, $N-C=S$, $N=N$, $-CH_2-CH-O-$, and the like. Among them, representative compounds are alkynediol, such as 2-butyne-1,4-diol, and coumarin. In the present invention, the crystal orientation ratio

5 $I_{(200)}/I_{(111)}$ of the endless metal belt can be restricted to a desired range by adding alkynediol to a nickel sulfamate plating bath. More specifically, there is a method of adjusting the crystal orientation ratio by using, for example, aromatic sulfonate as the

10 primary brightener and using alkynediol, for example, 2-butyne-1,4-diol, as the secondary brightener. However, the present invention is not limited to a specific method, but any method can be adopted as long as it can restrict the crystal orientation ratio

15 $I_{(200)}/I_{(111)}$ to the above range. To restrict the carbon content of the metal base material to a desired range, a method of regulating the kinds and the addition amount of the brighteners is preferred.

(Manufacturing Method)

20 The metal belt is formed by electroforming, using a nickel plating bath, such as Watt bath mainly containing nickel sulfate and nickel chloride and Sulfamate bath mainly containing nickel sulfamate. Electroforming is a method of providing thick plating

25 on a surface of a matrix, and exfoliating it from the matrix to obtain a product. To obtain the metal belt, a cylinder made of stainless steel, brass, or aluminum,

etc. is used as the matrix, and a nickel plating film is formed on a surface of the matrix by using a nickel plating bath.

If the matrix is a nonconductor such as silicone resin and gypsum, it is subjected to conductivity treatment by using graphite, copper powder, silver mirror, and sputtering, etc. In electroforming to a metal matrix, to facilitate exfoliation of the nickel plating film, an exfoliation treatment is preferably performed, for example, formation of an exfoliation film, such as an oxide film, compound film and graphite-powder-applied film, on the surface of the matrix.

The nickel plating bath comprises a nickel ion source, anode resolvent, pH buffering agent, and other additives. Examples of the nickel ion source are nickel sulfamate, nickel sulfate, and nickel chloride. In Watt bath, nickel chloride functions as the anode resolvent, and ammonium chloride and nickel bromide are used as the anode resolvent in the other nickel baths.

Nickel plating is generally performed within the pH range of 3.0 to 6.2. To adjust the pH to be within the desired range, a pH buffering agent such as boric acid, formic acid, and nickel acetate is used. As other additives, brighteners, pit preventing agent, and internal-stress reducer are used, for the purpose of smoothing, preventing pits, making crystals finer,

and reducing the residual stress.

With respect to the composition of the nickel plating bath, for example, the composition of a sulfamate bath comprises 300-600 g/L of nickel sulfamate, 0-30 g/L of nickel chloride, 20-40 g/L of boric acid, a proper amount of surface active agent, and a proper amount of brightners. The pH of the bath is preferably 3.5 to 4.5, and the temperature of the bath is preferably 40 to 60℃. The current density is preferably 0.5 to 15 A/dm^2, and 3 to 40 A/dm^2 in a bath of a high concentration.

(Release Layer)

The release layer 3 is generally formed of heat-resistant resin having releasing property, such as fluorocarbon resin, polyimide resin, and polyamideimide resin. If desired, it can be a rubber layer or rubber composition layer having releasing property and elasticity, such as silicone rubber, fluorine rubber, or a mixture of fluorine rubber and fluorocarbon resin, and a mixture of silicone rubber and fluorocarbon resin. In the case of adopting the latter, an elastic layer can be omitted, since the release layer has elasticity.

If the release layer is a heat-resistant resin layer, the thickness of the layer is generally 0.1 to 150 μm, preferably 1 to 100 μm, and more preferably 5 to 50 μm. If the release layer is a rubber layer

having elasticity, the thickness thereof is 10 μm to
5 mm, preferably 20 μm to 3 mm. The width and the
external diameter of the coated belt can be set
according to use of the belt.

5   As described above, the release layer is usually
formed of heat-resistant resin having releasing
property, such as fluorocarbon resin. If desired,
it can be a rubber layer or rubber composition layer
having releasing property and elasticity, such as
10   silicone rubber, fluorine rubber, or a mixture of
fluorine rubber and fluorocarbon resin, and a mixture
of silicone rubber and fluorocarbon resin.

As the heat-resistant resin, preferred is a resin
having such heat resistance that it does not melt or
15   softened and does not substantially deteriorate, even
if it is continuously used at a temperature of 150℃ or
more. On the assumption that the coated belt of the
present invention is used as a fixing belt and the like
under high-temperature conditions, the heat-resistant
20   resin is more preferably a synthetic resin having heat
resistance and being continuously usable at a high
temperature of 200℃ or more. Examples of such a heat-
resistant resin are fluorocarbon resin, polyimide
resin, polyamideimide resin, polyethersulfone resin,
25   polyetherketone resin, polybenzimidazole resin,
polybenzoxazole resin, polyphenylenesulfide resin,
and Bismaleimide resin. Among them, fluorocarbon resin

is particularly preferable for its excellent heat resistance and releasing property.

Examples of fluorocarbon resin are polytetrafluoroethylene (PTFE), tetrafluoroethylene/perfluoroalkylvinylether copolymer (PFA), tetrafluoroethylene/hexafluoropropylene copolymer (FEP), ethylene/tetrafluoroethylene copolymer (ETFE), polychlorotrifluoroethylene (PCTFE), ethylene/chlorotrifluoroethylene copolymer (ECTFE), and polyvinylidene fluoride (PVDF), etc.

Each of the fluorocarbon resins can be used singly, or at least two of them can be used in combination. If the coated belt is used as a fixing belt or a pressing belt, PTFE and PFA are preferred among the fluorocarbon resins, in view of the heat resistance. Further, PFA is more preferred, since it has flowability in molten state and a fluorocarbon resin coating having excellent surface smoothness can easily be obtained.

Although the fluorocarbon resin can be used in the form of liquid fluorocarbon resin coating, it is preferably used in powder form (powder coating) to improve formability and releasing property. Although the average grain size of the fluorocarbon resin powder is not particularly limited, it is preferably not more than 10 μm to form a thin coating with even thickness by means of powder coating. The lower limit of

the average grain size is generally around 1 μm.
In particular, it is preferred to use PFA powder having
an average grain size of 10 μm or less. To coat
fluorocarbon resin powder, various general-purpose

5   powder coating methods are available. Among them,
an electrostatic coating (electrostatic powder
spraying), in which powder is charged with electricity
and applied, is preferably used since it can form
a uniform and firm powder coating layer.

10   The fluorocarbon resin is applied onto the
endless metal belt base material, and then baked by
a publicly-known method. If an elastic layer is
disposed between the fluorocarbon resin layer and the
endless metal belt, fluorocarbon resin may be applied

15   and baked, after an elastic layer is formed on the
endless metal belt base material or endless metal belt
having internal surface coated in advance. However,
in a preferred method, a thin (not more than 30 μm)
fluorocarbon resin tube whose internal surface is

20   treated in advance (to improve its adhesiveness) is
fitted in a cylindrical mold so as not to become
wrinkled, and an endless metal belt base material on
which an elastic layer is formed or an endless metal
belt having a coated internal surface is held in a core

25   of the columnar or cylindrical mold and inserted into
the fluorocarbon resin tube. Then, adhesive (liquid
silicone rubber) is injected into the space between

the tube and the elastic layer, smoothed and heated. The thickness of the fluorocarbon resin coating after baking is generally 0.1 to 150 μm, preferably 1 to 100μm, and more preferably 5 to 50 μm. If the elastic layer is disposed under the release layer the thickness of the fluorocarbon resin coating can be set to 30 μm or less, to make full use of flexibility of the elastic layer.

By using fluorocarbon resin having a tube form, a fluorocarbon resin layer having excellent surface smoothness and releasing property can be formed.

(Elastic Layer)

The elastic layer 2 is not indispensable, but an optional constituent element in the present invention. Therefore, the coated belt 10 may have a three-layer structure of the release layer 3/metal base material 1/sliding layer 4, or a two-layer structure of release layer 3/metal base material 1. In particular, if the belt is used for heating and fixing of monochrome images, in which the amount of toner mounted on the transfer member is small and unevenness of the toner layer is relatively low, the coated belt 10 may have a three-layer or two-layer structure with no elastic layer 2.

If the elastic layer 2 is provided, although one elastic layer suffices, two or more layers may be provided as the occasion demands. The material of the

elastic layer 2 is preferably a rubber material having
excellent heat resistance, such as silicone rubber and
fluorine rubber. It is also possible to use a rubber
composition obtained by mixing fluorocarbon resin with

5 rubber such as silicone rubber and fluorine rubber.
Using such material adheres a plurality of elastic
layers to each other more closely.

   The thickness of the elastic layer 2 (if there
are two or more elastic layers, the total thickness

10 thereof) can be set according to its use, and is not
limited to a specific value. If it is used in a fixing
belt and the like of an image forming apparatus, the
thickness is generally 20 to 1000 μm, preferably 150
to 450 μm.

15 The rubber material used for formation of the
elastic layer 2 is a rubber having excellent heat
resistance, such as silicone rubber and fluorine
rubber. The term "heat-resistant rubber" indicates
rubber having enough heat resistance to withstand

20 continuous use at a fixing temperature, if the coated
belt is used as the fixing belt and the pressing belt.
Specifically, a rubber material is preferred which
neither melts nor is softened and does not
substantially deteriorate, even if it is continuously

25 used at a temperature of 150°C or more.

   The rubber material is preferably a millable or
liquid silicone rubber, fluorine rubber, or a mixture

thereof, since they have particularly excellent heat
resistance. Examples of the rubber material are:
silicone rubber such as dimethylsilicone rubber,
fluorosilicone rubber, methylphenylsilicone rubber,
and vinyl silicone rubber; and fluorine rubber such
as fluorine vinylidene rubber,
tetrafluoroethylene-propylene rubber,
tetrafluoroethylene-perfluoromethylvinylether rubber,
phosphazene-based fluorine rubber, and fluoropolyether
rubber. Among them, liquid silicone rubber which is
easily injected into the mold is preferably used.
The rubbers can be used singly, or two or more rubbers
can be used in combination.

(Sliding Layer)

If the sliding layer 4 is formed on the internal
peripheral surface of the belt, polyimide varnish is
applied to the internal surface of the endless metal
belt base material. After drying, the varnish is
heated and thereby dehydrated and the ring is closed
(imidized). If the heat-resistant resin is
thermoplastic resin, a solution thereof is applied
and dried. The thickness of the sliding layer 4 is
preferably adjusted in the same manner as in the case
of the release layer 3. The thickness of the sliding
layer 4 is 5 μm to 100 μm, especially preferably
10 μm to 60 μm. If the sliding layer 4 is excessively
thin, the durability may be insufficient. If the

sliding layer 4 is excessively thick, the rise time is increased. The sliding layer 4 may contain a sliding agent, such as fluorocarbon resin powder, graphite, and molybdenum disulfide, as the occasion demands.

5   (Example 1)

As a metal base material of Example 1, a metal belt sample A shown in FIG. 1 with an internal diameter of 34 mm and thickness of 50 μm was manufactured. Then, silicone rubber as the elastic layer 2 with

10   a thickness of 300 μm, and a PFA tube as the release layer 3 with a thickness of 30 μm were layered thereon, with a primer intervening between layers. Further, a polyimide resin layer with a thickness of 10 μm was layered thereon as the sliding layer 4, and

15   a coated belt was obtained.

In manufacturing of the metal base material (metal belt), first, an aqueous solution bath containing 500g/l of nickel sulfamate tetrahydrate and 35 g/l of boric acid was prepared as the electrolytic bath.

20   Then, the aqueous solution was subjected to electrorefining with a low current, while being filtered by using a 0.5μm filter in a vessel filled with activated carbon. Next, the activated carbon was removed from the vessel, a pit inhibitor of a necessary

25   amount was added to the solution, and then 0.3 g/l of 1,3,6-naphthalene-trisulfonic acid trisodium salt serving as the primary brightener and 100 mg/l of

2-butyne-1,4-diol serving as the secondary brightener were added to the solution.

By using the electrolytic bath obtained, electroforming was performed at a predetermined bath temperature and a current density of 10.5 A/dm^2, with a stainless matrix used as a cathode, and thereby an electrodeposited member having an internal diameter of 34 mm and thickness of 50 μm was formed. After being washed by pure water, the electrodeposited member was removed from the matrix, and used as the metal base material.

The crystal orientation ratio $I_{(200)}/I_{(111)}$ of the obtained metal belt (sample A) was obtained by measuring the X-ray diffraction intensities of a plane (200) (d value = 0.17620 nm) and a plane (111) (d value = 0.20340 nm) by means of wide-angle X-ray diffraction method with "RINT 2100 Ultima$^+$/PC (analysis software: JADE)" (trade name), which is an X-ray diffractometer manufactured by RIGAKU DENKI Corporation, and obtaining a rate of integral intensity of them.

The carbon content and sulfur content in the metal belt were determined by method of high-frequency heating and combustion in oxygen flow/infrared-radiation. The method of high-frequency heating and combustion in oxygen flow/infrared-radiation is a method, in which a sample is heated and oxidized in an oxygen flow to oxidize carbon in the sample to

carbon dioxide and carbon monoxide and oxidize sulfur in the sample to sulfur dioxide, the flow is introduced into an infrared detector at a fixed flow rate, and the carbon concentration in the sample is calculated

5 on the basis of the detected carbon dioxide and carbon monoxide, and the sulfur concentration is calculated on the basis of the detected sulfur dioxide.

A calibration curve is formed by measuring a blank and a reference material. The carbon content of sample A

10 of Example 1 was 0.030 wt%, and the crystal orientation ratio thereof was 113.

Table 1

Sample	SN (g/L)	BA (g/L)	Primary brightner (g/L)	Secondary brightner (g/L)	Current density (A/dm2)	Electro-deposition stress (releasing property)	Carbon content (wt%)	Crystal orientation ratio	Number of repetition durability times	Evaluation
A (Example 1)	500	35.0	0.3	100	10.5	Passed	0.030	113	about 250,000	○
B (Example 2)	500	35.0	0.3	120	10.5	Passed	0.034	132	about 390,000	○
C (Example 3)	500	35.0	0.3	180	10.5	Passed	0.049	169	1,000,000	○
D (Example 4)	500	35.0	0.3	180	8.9	Passed	0.061	246	1,000,000	○
E (Example 5)	500	35.0	0.3	180	7.9	Passed	0.070	198	1,000,000	○
F (Example 6)	500	35.0	0.3	180	5.8	Passed	0.084	147	1,000,000	○
G (Example 7)	500	35.0	0.3	180	5.3	Passed	0.088	114	1,000,000	○
H (Comparative Example 1)	500	35.0	0.3	0	10.5	Passed	0.0076	15	about 130,000	×
I (Comparative Example 2)	500	35.0	0.3	60	10.5	Passed	0.019	50	about 130,000	×
J (Comparative Example 3)	500	35.0	0.3	180	0.5	Not passed	0.14	Unmeasurable	Unmeasurable	×

SN: nickel sulfamate tetrahydrate

BA: boric acid

Primary brightener: 1,3,6-naphthalene-trisulfonic acid trisodium salt

Secondary brightener: 2-butyne-1,4-diol

(Example 2)

As a metal base material of Example 2, a metal belt sample B shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm.

The metal belt was manufactured under the same conditions as those of Example 1, except the addition amount of the second brightener. In manufacturing of sample B, 120 mg/l of 2-butyne-1,4-diol was added as the second brightener. The carbon content of the sample B was 0.034 wt%, and the crystal orientation ratio thereof was 132.

(Example 3)

As a metal base material of Example 3, a metal belt sample C shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm.

The metal belt was manufactured under the same conditions as those of Example 1, except the addition amount of the second brightener. In manufacturing of sample C, 180 mg/l of 2-butyne-1,4-diol was added as the second brightener. The carbon content of the sample C was 0.049 wt%, and the crystal orientation ratio thereof was 169.

(Example 4)

As a metal base material of Example 4, a metal belt sample D shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm.

The metal belt was manufactured under the same

conditions as those of Example 1, except the addition
amount of the second brightener and the current
density. In manufacturing of sample D, 180 mg/l of
2-butyne-1,4-diol was added as the second brightener.
The current density was set to 8.9 A/dm^2. The carbon
content of the sample D was 0.061 wt%, and the crystal
orientation ratio thereof was 246.

(Example 5)

As a metal base material of Example 5, a
metal belt sample E shown in Table 1 was manufactured
with an internal diameter of 34 mm and a thickness of
50 μm.

The metal belt was manufactured under the same
conditions as those of Example 1, except the addition
amount of the second brightener and the current
density. In manufacturing of sample E, 180 mg/l of
2-butyne-1,4-diol was added as the second brightener.
The current density was set to 7.9 A/dm^2. The carbon
content of the sample E was 0.070 wt%, and the crystal
orientation ratio thereof was 198.

(Example 6)

As a metal base material of Example 6, a
metal belt sample F shown in Table 1 was manufactured
with an internal diameter of 34 mm and a thickness of
50 μm.

The metal belt was manufactured under the same
conditions as those of Example 1, except the addition

amount of the second brightener and the current density. In manufacturing of sample F, 180 mg/l of 2-butyne-1,4-diol was added as the second brightener. The current density was set to 5.8 A/dm^2. The carbon

5   content of the sample F was 0.084 wt%, and the crystal orientation ratio thereof was 147.

(Example 7)

As a metal base material of Example 7, a metal belt sample G shown in Table 1 was manufactured with an

10   internal diameter of 34 mm and a thickness of 50 μm.

The metal belt was manufactured under the same conditions as those of Example 1, except the addition amount of the second brightener and the current density. In manufacturing of sample G, 180 mg/l of

15   2-butyne-1,4-diol was added as the second brightener. The current density was set to 5.3 A/dm^2. The carbon content of the sample G was 0.088 wt%, and the crystal orientation ratio thereof was 114.

(Comparative Example 1)

20   As a metal base material of Comparative Example 1, a metal belt sample H shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm. In the Comparative Example 1, 2-butyne-1,4-diol, the second brightener, was not

25   added. The other conditions thereof were the same as those of Example 1. The carbon content of the sample H was 0.0076 wt%, and the crystal orientation ratio

thereof was 15.

(Comparative Example 2)

As a metal base material of Comparative Example 2, a metal belt sample I shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm. In the Comparative Example 2, 60 mg/l of 2-butyne-1,4-diol was added as the second brightener. The other conditions thereof were the same as those of Example 1. The carbon content of the sample I was 0.019 wt%, and the crystal orientation ratio thereof was 59.

(Comparative Example 3)

As a metal base material of Comparative Example 3, a metal belt sample J shown in Table 1 was manufactured with an internal diameter of 34 mm and a thickness of 50 μm. In the Comparative Example 3, 180 mg/l of 2-butyne-1,4-diol was added as the second brightener, and the current density was set to 0.5 A/dm^2. No sound electrodeposited member was formed in Comparative Example 3, and thus the crystal orientation ratio of sample J couldn't be measured. The carbon content of the sample J was 0.14 wt%.

A test piece 20 shown in FIG. 2 was extracted from each of the endless metal belts obtained as described above, and each test piece was subjected to a durability test. As a test piece 20 for a metal material tensile test, a test piece of No. 13B defined

under JIS Z2201 was used. The following are dimensions

of the parts of the test piece 20.

Parallel portion width W1: 12.5 mm

Parallel portion length L: 60 mm

5   Bench marks interval: 50 mm

Shoulder portion radius R: 20 mm

Grip portion width W2: 20 mm

The following are conditions of the durability

test.

10   Maximum repeated load: 550 N/mm^2

Minimum repeated load: 80 N/mm^2

Atmosphere temperature: 250℃

Repetition cycle: 15 Hz

As shown in FIG. 3 and Table 1, the number of

15   repetition durability times of each sample was obtained

by the fatigue test at high temperature. The numbers

of repetition durability times of samples H and I of

comparative examples 1 and 2, having the crystal

orientation ratio $I_{(200)}/I_{(111)}$ of less than 50, were

20   about 130,000, which was small and did not reach the

acceptable level, 200,000. In the meantime, the number

of repetition durability times of samples A-G of

Examples 1-7, having the crystal orientation ratios

$I_{(200)}/I_{(111)}$ of 113, 132, 169, 246, 198, 147 and 114,

25   respectively, were about 250,000, 390,000, not less

than 1,000,000, not less than 1,000,000, not less than

1,000,000, not less than 1,000,000, and not less than

1,000,000, respectively, which were much larger than 200,000 times, the acceptable level. Samples having the crystal orientation ratio of around 100 tend to have varying number of repetition durability times. As the crystal orientation ratio of the belt increases, the number of repetition durability times thereof tends to increase and be less variable. The crystal orientation ratio of sample J in Comparative Example 3 could not be measured, since the film was not formed soundly in sample J.

As shown in FIG. 4 and Table 1, in Examples 1-7, the carbon contents (wt%) of samples A, B, C, D, E, F and G were 0.030, 0.034, 0.049, 0.061, 0.070, 0.084, and 0.088, respectively. The numbers of repetition durability times of the samples were good as described above.

Further, with respect to the relationship between the carbon content and the orientation ratio, as shown in FIG. 5 and Table 1, the crystal orientation ratio increased gradually, 113, 132, 169, and 246, as the carbon content (wt%) gradually increased, 0.030, 0.034, 0.049 and 0.061, among Examples 1-4 (samples A, B, C and D). However, when the carbon content (wt%) further increased, 0.070, 0.084 and 0.088 as among Examples 5-7 (samples E, F and G), the crystal orientation ratio gradually decreased, 198, 147, and 114.

In the meantime, the carbon contents of

Comparative Examples 1 and 2 (samples H and I) were 0.0076% and 0.019%, respectively, and their crystal orientation ratios were small, 15 and 50, respectively. The carbon content (wt%) of Comparative Example 3 was 0.14%, and its crystal orientation ratio could not be measured.

In each of Examples 1-7, as described above, it was found that the number of repetition durability times greatly exceeded the allowable level, 200,000 times, and that there was an obvious correlation between the carbon content and the orientation ratio.

The above are the results of the evaluation test performed for the metal belt. A coated belt having the metal belt as the metal base material can be evaluated by the same test.

The belt of the present invention has an excellent durability and a long life, since it has the crystal orientation in which the crystal orientation ratio $I_{(200)}/I_{(111)}$ is from 80 to 250 inclusive 80 and 250 and the plane (200) is preferentially grown. Further, since the carbon content of the belt of the present invention is set to a specific range, the belt has an excellent durability, enables easy removal of the electroformed product thereof from the matrix, and avoids occurring of partial exfoliation of the electroformed member from the matrix. Therefore, the metal belt and the coated belt of the present invention

are suitably used as a fixing belt in an image forming
apparatus, such as an electrophotographic copying
machine.